# ACOUSTIC PERFORMANCE OF HYBRID RENEWABLE POLYURETHANE BLENDED WITH SYNTHETIC EPOXY FOAM WITH AND WITHOUT TITANIUM DIOXIDE FILLER UPON IRRADIATED EXPOSURE

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## DEDICATION

"*Special dedicated to my beloved family, my lecturers and my friends who always gave me support and encouragement*"

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# ABSTRACT

Waste cooking oils are problematic disposal especially in the developed countries. Options for disposing of waste cooking oil are limited. Therefore, in this research, vegetable waste cooking oil is used as raw material to produce renewable polymer foam as an alternative product. This is started with the crosslinking of renewable monomer with isocyanate to generated renewable polymer foam. Further process is comprised with the addition of synthetic epoxy or titanium dioxide ($TiO_2$) by different ratio (wt/wt) of renewable monomer. Fabricated samples was divided into three types of foam namely as epoxy foam (EF), renewable polymer foam (RF) loaded with different percentage loading of titanium dioxide ($TiO_2$) as filler namely as $EF_{1-3}$ and $RF_{1-3}$ and epoxy/renewable polymer foam (ERF). At prolonged UV irradiation exposure, the density of all specimens was increase but the pore sizes were decreased as the percentages of $TiO_2$ were increased. For EF, RF and EFR samples shows highest at frequency absorption level (Hz) of α at each individual category with 0.965 at 2943 Hz, 0.995 at 3106 Hz, 0.945 at 3684 Hz. The lowest α at frequency absorption level (Hz) of EF, RF and ERF is 0.878 at 3181 Hz, 0.823 at 3184 Hz, 0.876 at 3526 Hz respectively. Meanwhile for composite samples $EF_{1-3}$ and $RF_{1-3}$ shows higher α at absorption frequency level (Hz) of each individual category with 0.968 at 3928 Hz, 0.998 at 3728 Hz and lowest α at frequency absorption level (Hz) of 0.836 at 3512 Hz, 0.878 at 3915 Hz respectively. As a general remark, the highest loading of $TiO_2$ show $RF_3$ resulted in reduced of cell sizes after UV irradiation exposure and contributed the higher α. Thus, the morphological study of SEM was revealed that $RF_3$ have smallest cell sizes after UV irradiation exposure with 681 μm diameter. In other words, the decrement in cell sizes of higher $TiO_2$ loading was improved the sound absorption property at prolonged UV irradiation hours 1000 hours.

# ABSTRAK

Sisa minyak masak adalah bahan buangan yang menyumbang kepada masalah pelupusan bagi di negara-negara membangun. Pilihan untuk melupuskan sisa minyak masak adalah terhad. Dalam kajian ini, sisa minyak masak sayuran digunakan sebagai bahan mentah untuk menghasilkan span polimer yang boleh diperbaharui. Ianya bermula dengan silangan monomer dan isosianat untuk menghasilkan span polimer yang diperbaharui. Proses selanjutnya terdiri dengan penambahan sintetik epoxy atau titanium dioksida ($TiO_2$) dengan nisbah yang berbeza (berat/berat) untuk monomer yang diperbaharui. Penghasilan samples dibahagikan kepada tiga jenis iaitu span epoksi (EF), span polimer yang diperbaharui yang dicampurkan dengan perbezaaan peratusan titanium dioksida ($TiO_2$) yang dinamakan $EF_{1-3}$ dan $RF_{1-3}$ dan epoksi/span polimer yang diperbaharui (ERF). Pada pendedahan sinaran ultra (UV), ketumpatan semua sample telah meningkat tetapi saiz liang telah berkurang mengikut peningkatan peratusan $TiO_2$. Untuk EF, RF dan ERF sample menunjukkan tahap tertinggi penyerapan frekuensi (Hz) bagi α pada setiap kategori adalah sebanyak 0.965 pada 2943 Hz, 0.995 pada 3106 Hz, 0.945 pada 3684 Hz. Penyerapan frekuensi (Hz) terendah bagi α untuk EF, RF, ERF masing-masing adalah 0.878 pada 3181 Hz, 0.823 pada 3184 Hz, 0.876 pada 3526 Hz. Manakala, bagi sample komposit $EF_{1-3}$ dan $RF_{1-3}$ tahap tertinggi penyerapan frekuensi (Hz) bagi α pada setiap kategori adalah 0.968 pada 3928 Hz, 0.998 pada 3728 Hz dan penyerapan frekuensi (Hz) terendah bagi α masing-masing adalah 0.836 pada 3512 Hz, 0.878 pada 3915 Hz. Umumnya, peningkatan $TiO_2$ menunjukkan penurunan bilangan saiz liang selepas pendedahan sinaran ultra (UV) dan menyumbang kepada kenaikkan α. Kemudian, kajian morfologi SEM menunjukkan span $RF_3$ menghasilkan saiz sel diameter terkecil selepas pendedahan sinaran UV iaitu 681 µm. Kesimpulan, penurunan sel saiz pada peratusan tertinggi $TiO_2$ dapat membantu penyerapan bunyi dan pada kenaikkan penyinaran UV pada 1000 jam.

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF SYMBOLS

| | | |
|---|---|---|
| $\alpha$ | - | Sound absorption coefficient or viscoelastic parameter |
| $\rho$ | - | Density |
| W, M, m | - | Total mass or total riding mass |
| EF | - | 100 % Epoxy with 0 % Renewable monomer |
| RF | - | 0 % Epoxy with 100 % Renewable monomer |
| $ERF_{80/20}$ | - | 80 % Epoxy with 20 % Renewable monomer |
| $ERR_{60/40}$ | - | 60 % Epoxy with 40 % Renewable monomer |
| $ERF_{40/60}$ | - | 40 % Epoxy with 60 % Renewable monomer |
| $ERF_{20/80}$ | - | 20 % Epoxy with 80 % Renewable monomer |
| $EF_1$ | - | 1 % of $TiO_2$ for Epoxy |
| $EF_2$ | - | 2 % of $TiO_2$ for Epoxy |
| $EF_3$ | - | 3 % of $TiO_2$ for Epoxy |
| $RF_1$ | - | 1 % of $TiO_2$ for Renewable monomer |
| $RF_2$ | - | 2 % of $TiO_2$ for Renewable monomer |
| $RF_3$ | - | 3 % of $TiO_2$ for Renewable monomer |
| $W_W$ | - | Mass of an immersed and suspended specimen in air. |
| $W_D$ | - | Mass of air dried specimen |
| $W_S$ | - | Mass of immerse and suspend specimen in liquid |

## LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| UV | - | Ultraviolet |
| $TiO_2$ | - | Titanium dioxide |
| PU | - | Polyurethane |
| PET | - | Polyethylene Terephthalate |
| wt. | - | weight |
| UTHM | - | Universiti Tun Hussein Onn Malaysia |
| SEM | - | Scanning Electron Microscopy |
| ASTM | - | American Society for Testing and Materials |
| MDI | - | Methylene Diphenyl Diisocyanate |
| NRC | - | Noise Reduction Coefficient |
| PLA | - | Polylactic asid |
| $CaCO_3$ | - | Calcium Carbonate or Calcite |
| BP | - | Biodegradable polymer |
| $CO_2$ | - | Carbon Dioxide |
| TAG | - | Triacylglycerol |
| $CNF_S$ | - | Carbon nanofibres |
| $CNT_S$ | - | Carbon nanotube |
| OH | - | Hydroxide |
| O | - | Oxygen |
| CFD | - | Compression force deflection |
| MWCNTs | - | Multiwalled carbon nanotube |
| f-MWCNTs | - | Functionalized multiwalled carbon nanotube |
| FGS | - | Functionalized graphene sheets |
| NA-MMT | - | Sodium montmorillonite |

| | | |
|---|---|---|
| EF | - | 100 % Epoxy 0 % Renewable monomer, 0.5 % of isocyanate |
| RF | - | 80 % Epoxy 20 % Renewable monomer, 0.5 % of isocyanate |
| $ERF_{80/20}$ | - | 60 % Epoxy 40 % Renewable monomer, 0.5 % of isocyanate |
| $ERF_{60/40}$ | - | 40 % Epoxy 60 % Renewable monomer, 0.5 % of isocyanate |
| $ERF_{40/60}$ | - | 20 % Epoxy 80 % Renewable monomer, 0.5 % of isocyanate |
| $ERF_{20/80}$ | - | 0 % Epoxy 100 % Renewable monomer, 0.5 % of isocyanate |
| $EF_1$ | - | 100 % of Epoxy, 0.5 % of isocyanate, 1.0 % of $TiO_2$ |
| $EF_2$ | - | 100 % of Epoxy, 0.5 % of isocyanate, 2.0 % of $TiO_2$ |
| $EF_3$ | - | 100 % of Epoxy, 0.5 % of isocyanate, 3.0 % of $TiO_2$ |
| $RF_1$ | - | 100 % of Renewable monomer, 0.5 % of isocyanate, 1.0 % of $TiO_2$ |
| $RF_2$ | - | 100 % of Renewable monomer, 0.5 % of isocyanate, 2.0 % of $TiO_2$ |
| $RF_3$ | - | 100 % of Renewable monomer, 0.5 % of isocyanate, 3.0 % of $TiO_2$ |

# LIST OF APPENDICES

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of study

Polymeric foams are important and versatile material due to their outstanding strength-to-weight ratio, resilience, electrical, thermal and acoustic insulating properties, among other characteristics. Polyurethane is one of the largest and most versatile families of polymer (Verdego *et al.,* 2009). Some notable applications of this foam material include mattresses, upholstery, furniture, footwear and textiles in our homes and office, and as packing, appliances, electronics, machinery and foundry, and as cushioning material in automobiles as well as in the industries as shown in Figure 1.1.

Figure 1.1: Major application of flexible PU foam (Polyurethane Foam Association 1992, 1996 and 1997)

Furthermore, as refer to Klempner and Sendijarevic (2004), polymeric foams shows excellence in being lightweight, strength to weight ratio performance, and most importantly, if offers a degree of comfort, protection, and utility not matched by other single material. By proper choice of raw materials, additive and manufacturing technology, the properties of flexible PU foam can be changed to satisfy desired application. Generally, the characteristic of flexible PU foam can be soft or rigid chemical composition of raw material, in particular polyol and isocyanate.

During the formation of flexible PU foam, polyol and isocyanate are mixed to form polyurethane linkage. However, due to the fluctuation of oil prices, these petro-chemical feed stocks would rise in price and this in fact could influence the production cost of automotive seats (Latinwo *et al.,* 2010a).

Various experiment aimed in improving both the mechanical properties and cost effectiveness of renewable polymer foam has been conducted. One attempt of achieving this involved the chemical modification of its structure. Another modification involved the use of fillers to achieve flexible polyurethane / filler composite formation. Inorganic filler materials are available as nano-, micro-, and macro-scale crystals (Latinwo *et al.,* 2010b). According Sant'anna *et al.,*(2008), among the inorganic material utilized as filler, notable ones include: calcium carbonate, aluminium hydroxide, silica, titanium dioxide and talc. Some of the organic materials more commonly used are carbon black and natural fibers. Their effects on plastic foam material have been known to strongly depend on their sizes, aspect ratio, hybrid morphology, and dispersion quality. It is also well known that fillers increase cell density and decrease cell size. By affecting the macroscopic cell geometry, it can act as reinforcement material in polyurethane foam composites (Latinwo *et al.,* 2010b).

Therefore in this research, waste cooking oil has been utilized and is converted into monomer to produce renewable polymer foam. Renewable polymer foam with and without filler has been prepared to measure the mechanical and physical properties as well as it's resistance to ultraviolet (UV) irradiation exposure on the polymer foam. The properties of polymer were examined by using density test, Scanning Electron Microscope (SEM), UV test, and sound absorption test according to ASTM standard.

## 1.2 Problem Statement

In polymer industry, vegetable oil which represents a major potential source of chemicals has been utilized as an alternative feedstock for monomers. PU foam made from castor oil has existed for many years. Other oil such as soybean oil and rapeseed oil-based polyol has been used to make PU foams as well (Narine *et al.,* 2007).

In recent year, waste cooking oil has proven to be problematic material. Many people cannot solve the problem and did not know how to manage the problem instead of poured the oil into the drain or toilet. By recycling, the waste oils to substitute the petroleum based product as well as by improving the physical and mechanical properties and to reduce the environment pollution.

Furthermore, the use of renewable sources in the preparation of various industrial materials has been revitalized because of the environment concerns. Thus, the problem is to generate new idea and formulae either in automotive, packaging or building structure application by improving the performance of the foam. In specific, the problem of noise absorbing material in an automotive field or packaging needed alternative new material that can be used to replace substitute the existing products (Hulme and Goodhead, 2003).

Moreover, industries that produce flexible polyurethane foams use fillers to modify the material's properties as well as to reduce manufacturing cost. This is also to achieve dimensional stability, ease of retraction from the mold and service density (Usman *et al.,* 2012). A variety of particulate or fibrous fillers is used for cost reduction or mechanical properties improvement. The fillers are mainly include: silica, glass fibers, aluminium hydroxide or starch, $CaCO_3$, $Ca_3(PO_4)_2$, $CaSO_4$ and talc and even nanostructured fillers, such as carbon nanotube and nanoclays (Mello *et al.*,2009).

According to Usman *et al.,* (2012), when adding a filler to a polymer, it is to form a conjugated biphasic material. The tension applied to the polymeric matrix will be transferred to the disperse filler phase in which it's provide superior properties than the pure polymer. Thus, in this research, waste cooking oil monomer is used mixed with cross-linker to form renewable polymer foam. The selected filler such as titanium dioxide ($TiO_2$) is used to retard the degradation of polymeric materials as well as renewable polymer foam. The degradation of polymer could be occurs in a

wide variety of environment and service conditions, and very often limits the service lifetime.

In addition, polymer properties can be slightly affected during their processing, storage, and transportation, the most significant degradation occurs during expose to the environment. The aging is severe for polymeric materials because it combines the photo-physical and photo-chemical effect. The combine effects are due to ultraviolet (UV) irradiation with oxidative and hydrolytic effect of the outdoor environment (Xu *et al.,* 2011).

## 1.3 Hypothesis of research

i. To prove that a proper weight percentage (wt %) of epoxy foam and treated renewable polymer foam may offer good acoustic characteristic material.
ii. The epoxy foam and renewable polymer foam with and without $TiO_2$ have the potential to increase the dissipation of energy through absorption and sound.

## 1.4 Objective of research

i. To fabricated foam types samples namely as epoxy foam (EF), renewable polymer foam (RF) loaded with different percentage loading of titanium dioxide ($TiO_2$) as filler namely as $EF_{1-3}$ and $RF_{1-3}$ and epoxy/renewable polymer foam (ERF).
ii. To determine EF, RF and it's composite ($EF_{1-3}$ and $RF_{1-3}$) and ERF for density and porosity before and after UV irradiation exposure up to 1000 hours.
iii. To UV irradiate EF, RF and it's composite ($EF_{1-3}$ and $RF_{1-3}$) and ERF for sound and noise absorption.

## 1.5 Scope of research

i. Literature review on the fundamental of polymer foam fabrication process with different percentage ratio of renewable monomer blended with synthetic epoxy and titanium dioxide ($TiO_2$).
ii. The fabrication process is to prepare the epoxy foam (EF), renewable polymer foam (RF) loaded with different percentage loading of titanium dioxide ($TiO_2$) as filler namely as $EF_{1-3}$ and $RF_{1-3}$ and epoxy/renewable polymer foam (ERF).
iii. The physical and mechanical properties is determine on EF, RF and it's composite ($EF_{1-3}$ and $RF_{1-3}$) and ERF such as density, porosity and morphology characteristic by Scanning Electron Microscope (SEM).
iv. The acoustic sound and noise of UV irradiation exposure characteristic of EF, RF and it's composite ($EF_{1-3}$ and $RF_{1-3}$) and ERF by using sound absorption test according to ASTM standard is conducted.

## 1.6 Signification of research

i. This research intended to improve the sound absorbing properties of EF, RF and it's composite ($EF_{1-3}$ and $RF_{1-3}$) and ERF to be used in motor vehicle and packaging industry as well as any suitable application.
ii. To determine whether this research is able to increase the value of sound absorption coefficient (α) of EF, RF and it's composite ($EF_{1-3}$ and $RF_{1-3}$) and ERF
iii. The EF, RF and it's composite ($EF_{1-3}$ and $RF_{1-3}$) and ERF had been developed especially for automotive application, particularly in the focus on improving the comfort and tranquillity for a variety of uses.
iv. The EF, RF and it's composite ($EF_{1-3}$ and $RF_{1-3}$) and ERF can be replace as the component in application which offer a great production cost reduction due to the used of waste cooking oil.

## 1.7 Thesis organization

**CHAPTER 1** has highlighted the general introduction on this research, background of study, problem statement, hypothesis, objective, scope and its significance of research. It discussed the reason of research aimed in developing of FC using wood filler which can provide better sound absorption.

In **CHAPTER 2**, reviews of literature were focusing on epoxy, renewable polymer, foam production and its parameter and sound absorption coefficient.

**CHAPTER 3** shows the methodology that used to conduct the whole study. The technique density and porosity preparation, the physical and morphology characteristic test is described in details.

**CHAPTER 4** and **CHAPTER 5** cover the results and discussion of the experimental carried out from this research. The particles of foam are discussed in **CHAPTER 4**. It also shows the physical properties of the foam characterized using SEM and density measurement. In **CHAPTER 5**, the results of sound absorption before and after UV irradiation exposure were discussed in details.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

This chapter is discussed and reviewed previous studies from other researchers on development and characteristics of renewable polymer foam or blended with epoxy and titanium dioxide ($TiO_2$) as sound and noise absorption application. The testing methods used for evaluating the foam composite. It is to provide more information on in renewable polymer foam blended with synthetic epoxy foam and $TiO_2$ filler on its mechanical and physical properties for any new application.

## 2.2 Renewable polymer

Renewable polymer is polymers produced by living organisms. Since they are polymers, it is monomeric units are covalently bonded to form larger structure. There are three main classes of renewable polymer based on the differing monomeric units used and the structure of the renewable polymer formed. The resulting properties of these materials, from light weight with enhanced mechanical properties to greater sustainability, has meant a growing number of application in such areas as building, construction, automotive engineering and etc.

Renewable polymer can be sustainable, carbon neutral and are always renewable, because they are made from plant materials which can be grown year on year indefinitely. These plant materials come from agricultural non-food crops. Therefore, the use of renewable polymers would create a sustainable industry. In

contrast, the feed stock for polymers derived from petrochemicals will eventually run out (Mohanty *et al.*,1999). In addition, renewable polymer has the potential to cut carbon emission and reduce carbon dioxide ($CO_2$) quantities in the atmosphere. This is because $CO_2$ released as they degrade and can be reabsorbed by crops grown to replace them. Thus, this makes them close to carbon neutral.

Renewable polymers are biodegradable, and some are also compostable. Some renewable polymer is biodegradable: they are broken down into $CO_2$ and water by microorganisms. Some of these biodegradable renewable polymers are compostable: they can be put into an industrial composting process and will break down by 90 % within six months. Renewable polymer that does this can be marked with a 'compostable' symbol (Mohanty *et al.,* 1999). Packing marked with this symbol can be put into industrial composting processes and will break down within six months or less.

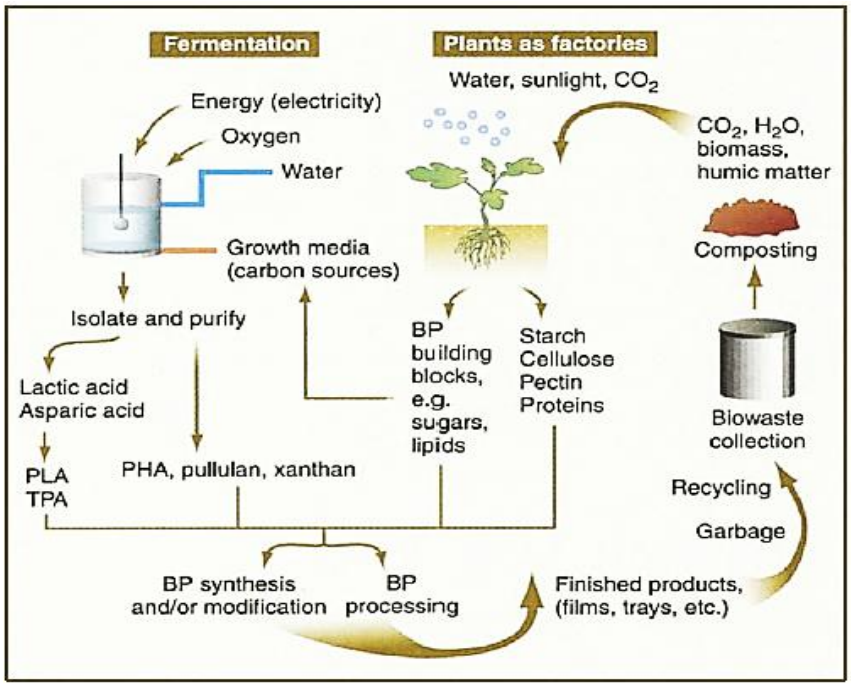



Figure 2.1: The Cyclic process of renewable polymer yielded through fermentation by agricultural processes, back into useful natural polymers (Mohanty *et al.,* 1999)

### 2.2.1 Renewable polymer from Renewable Resources

Large amount of plastic waste generated by industries poses serious environmental problem which may require for total degradation (Mantia *et al.,* 2008). An approach to decrease the solid waste is to substitute conventional material with biodegradable raw materials to reduce costs and to enhance the degradation of the final product. By renewable resources is meant agricultural product mainly from five principal crops: soybean, oil palm, rapseed, sunflower and coconut where the materials are synthesized by sunlight (Suresh *et al.,* 2007). Many researches have provided overviews of various partially and completely biodegradable resins and composites. Among these are various cellulose, protein and starch based materials, soy protein with low cost, easy availability and biodegradability.

The respect of the environment is a capital point in a sustainable development context. We should act in this way to preserve fossil resources and reduce the pollution of the Earth. The fabrication of industrial product must consume less energy and the raw materials must be in priority renewable resources, in particular from agriculture origin. Currently, two approaches are explored to minimize the impact of polymers on the environment:

i. The design of polymeric materials for long duration (e.g. aeronautic devices, construction materials, coating and containers), these materials must combine unalterability and be fashioned preferentially from renewable resources (e.g plant oil in thermoset, wood fiber in composites materials).
ii. Technological innovation designed for the production of polymer for short duration (e.g. disposable package, agricultural mulches, horticultural post, etc) must have the intention of fast biodegradability. Most biodegradability polymers belong to thermoplastics (e.g. poly (lactic acid), poly(hydoroxyalkanoate), poly(vinyl alchohol)) or plant polymers (e.g. cellulose and starch). Thermoplastics from polyolefin are not biodegradable, even if some of them have pro-oxidant additives making them photo and or thermo degradable (Lucas *et al.,*2008)

As an effort to develop polymers with high modulus and strength, more polymerizable functional groups are introduced onto the triglyceride molecules, resulting in high cross-linked network. The high cross-link density leads to polymers with high glass transition temperature, high modulus and high strength. However, with increasing cross-link density, the flexible character of the fatty acid chains changes as the mobility decreases, making them very brittle with poor resistance to crack initiation and propagation (Lu *et al.*, 2008).

The most well-know and widely used renewable biodegradable polymer is those from polysaccharides. The principal polysaccharide of interest to polymer chemists is starches, which is polymer of glucose. In addition to these, fibers, polylactic asid (PLA) and traicylglycerols of oils are of particular interst for the development of biodegradable industrial polymers.

Narine and Kong (2005) presented the starch is the most common polymer in plants. Large amounts of starch can be obtained from tubers such as potatoes, from cereals such as rice and from seeds such as corn. The starch molecule is heavily hydrated as it contains many exposed hydroxyl group, which form hydrogen bond on coming into contact with water. The starch –filled polyethylene films become porous after extraction of starch. This porous film can then be readily invaded by micro-organisms and rapidly saturated with oxygen, thereby increasing polymer degradation by biological and oxidative methods.

Alternatively waste cooking oil is used because of their potential to substitute petrochemical derivatives. Waste cooking oil usually has large amount of fatty acids, triglycerides, polymers and decomposition product (Guner et al., 2006). This residue poured down the drain, resulting in problem for waste water treatment or plant and energy loss, or it’s integrated into the food chain through animal feeds, thus becoming a potential cause of health problem.

The term "waste cooking oil" includes any vegetable oil (e.g., soybean oil, peanut oil, sunflower oil, linseed oil, coconut oil, cottonseed oil, canola oil, corn oil, safflower oil, walnut oil, castor oil, tung oil, etc.), animal fat (e.g., lard, fish oil, poultry fat, tallow, etc.), or by product or combination that has been heated to a high temperature or used in the preparation of food or other products.

Traditionally, these waste oils were used as an additive to animal feed. However, many harmful compounds are produced during the frying of vegetable oils. The European Union (EU), aware of this problem, banned the use of waste cooking

oils in the composition of animal feed in 2002. Most of the toxic compounds in the waste cooking oil are oxidation products from fatty acids, especially from polyunsaturated fatty acids (Bautista. L. F., Vicente, G., 2009).

Waste cooking oil can pose a pollution hazard if not handled properly. To prevent pollution of waterways and clogging of private and municipal drain systems, restaurants and other food preparation facilities typically storage of used cooking oil and employ sewage traps to filter grease out of waste water streams. Yellow and brown grease (also commonly referred to as trap grease, sewage grease, or black grease) are two forms of waste cooking oil that are readily available in bulk quantities. Yellow grease is of a slightly higher quality than brown grease and typically has a free fatty acid (FFA) content of between about 4 and 15 weight percent, while brown grease typically has a FFA content of up to about 60 weight percent. The current supply of yellow and brown grease exceeds the demand for these feedstocks.

Wang, Y., (2007) studied that waste cooking oils (WCO), which contain large amounts of free fatty acids produced in restaurants, are collected by the environmental protection agency in the main cities of China and should be disposed in a suitable way. Most restaurants, especially fast food restaurants, use commercial deep frying units to cook food items such as, for example, french fries, chicken, or fish by submersing the food items in hot cooking oil. The cooking oil (typically vegetable oil) has a limited shelf life, as it degrades and becomes contaminated by pieces of food as well as water and fats released from food during the cooking process. As a result, the cooking oil is changed on a regular basis.

Photodegradation changes the physical and optical properties of the plastic. The most damaging effects are the visual effect (yellowing), the loss of mechanical properties of the polymers, the changes in molecular weight and the molecular weight distribution for the same (Martin *et al.*, 2003; Hamid *et al.*, 1995; Andrady *et al.*, 1993). PE and PP films when exposed to solar UV radiation readily lose their extensibility, mechanical integrity and strength along with decrease in their average molecular weight (Abadal *et al.*, 2006).

In photo-oxidative degradation, mechanism involves auto-oxidation cycle comprising various steps shown in Figure 2.2

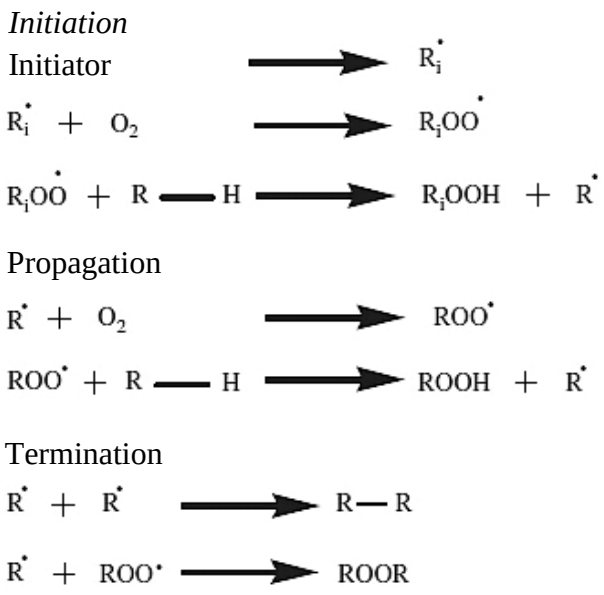



Figure 2.2: Mechanism of photodegradation (Hanaor and Sorrell, 2011).

The mechanism of photodegradation involves: (a) initiation, (b) propagation reaction, and (c) termination reactions.

Initiation is where the absorption of UV light that has sufficient energy to break the chemical bonds in the main polymer chain leads to the initiation of mechanism responsible for polymer degradation. It involves a radical chain mechanism for the formation of initial radical. Different initiation steps under varied conditions have been undertaken in different polymers.

The propagating reactions of auto-oxidation cycle are common to all carbon backbone polymers. These reactions lead to generation of hydroperoxide species and are not directly led to backbone cleavage but are the key intermediates to further reactions as shown in Figure 2.2. Hydroperoxide species generated in propagating step lead to backbone degradation through cleavage of hydroperoxide O-O bond followed by b-scission.

The termination of photodegradation is achieved by ‘mopping up’ the free radicals to create inert products. This occurs naturally by combining free radicals or assisted by using stabilizers in the plastic. Macroalkyl radicals may combine to give a crosslinked, branched or disproportionated product. Peroxyl radicals eventually

terminate by reaction with other radicals to give dialkyl peroxides, carbonyl species or alcohols.

Oxidation usually leads to increase brittleness and deterioration in strength. Generally, the mechanism of oxidative degradation is free radical formation and is initiated by the thermal or photolytic cleavage of bonds. The free radicals then react with oxygen to yield peroxides and hydroperoxides.

It should be indicated that irradiated polymeric materials undergo a series of oxidative reactions that lead to photochemical degradation (Zhang *et al.*, 1999) and with consequences like brittleness, loss of brightness, and color changes. Besides the cross-linking of the polymeric processes, a number of other changes may take place in polymeric chains during photodegradation (Rabek, 1995; Fechine, 2002).

### 2.2.2 Composition and important of vegetable oils in polymer production

Vegetable oils are one of the cheapest and most abundant, annually renewable natural resources available in large quantities from various oilseeds, and are now being used in an increasing number of industrial applications. Vegetable oils, such as soybean oil, palm oil and rapeseed oil are extracted primarily from the seeds of oilseed plants and have a wide variety of application: as food, fuels (biofuels), lubricants, paints, cosmetics, pharmaceuticals, plasticizers, and construction material. They are also attractive monomers for polymer chemistry due to their natural abundance and reactive functionality.

In recent years, there has been a growing trend in using vegetable oil as raw material in resin production. Among the advantages are:

i. The vegetable oils are renewable in perpetuity,
ii. Products derived from natural oils and fats are more readily biodegradable than the corresponding products made from petroleum and hence their impact on the environment is less, and
iii. The long fatty acid chains of vegetable oils impart desirable flexibility and toughness to otherwise brittle resin systems such as epoxy, urethane and polyester resins.

Fats and oils generally function in the latter capacity. Fats differ from oils only in that they are solid at room temperature, while oils are liquid. Fats and oils share a common molecular structure, which is represented in Figure 2.3.

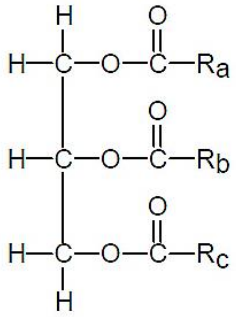
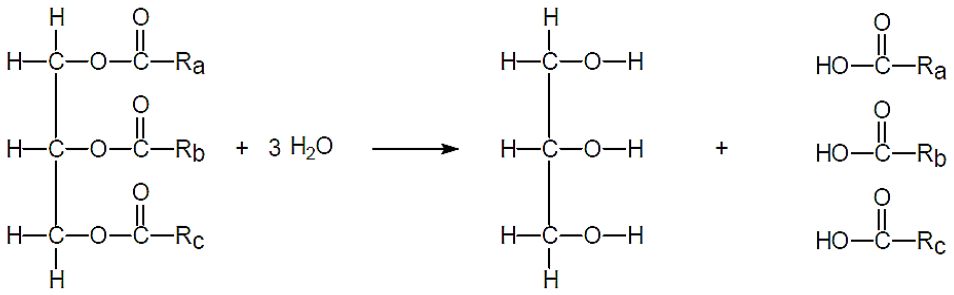


Figure 2.3: Chemical structure of fats and oils (Shakhashiri, 2008).

This structural formula in Figure 2.4 shows that fats and oils contain three ester functional groups which is tri-alcohol, glycerol (or glycerine). In the fatty acids, $R_a$, $R_b$, and $R_c$, represent groups of carbon and hydrogen atoms in which the carbon atoms are attached to each other in an unbranched chain (Shakhashiri, 2008).

According to Liu (2000), vegetable oils are triglycerides (tri-esters of glycerol with long chain fatty acids) with varying composition of fatty acids depending on the plant, season, crop and growing conditions. The word 'oil' is refers to the triglycerides that are in liquid form at room temperature.



triglyceride glycerol fatty acids

Figure 2.4: Hydrolysis reaction produces glycerol and fatty acids (Shakhashiri, 2008).

However, their use as monomers presents challenges due to their heterogeneous and variable structures. Indeed, it can be expensive to separate and extract the different triglycerides present because the oils are typically expressed in low concentrations and the composition of particular oil can vary seasonally. The key chemical building blocks of vegetable oils are triglycerides: triesters of glycerin and fatty acids as shown in Figure 2.5. Of the five commonly occurring fatty acids, two are saturated (palmitic and stearic) and three are unsaturated (oleic, linoleic, and linolenic) (Williams, *et al.*, 2008).

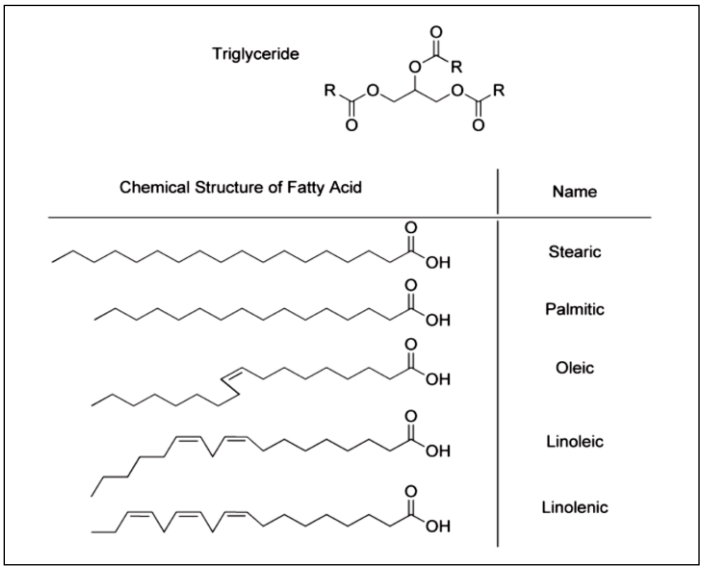



Figure 2.5: The structure of triglycerides and the five most common fatty acid substituents for vegetable oils (Williams *et al.*, 2008)

Vegetable oils are one of the most abundant biological sources and important raw materials for the production of bio-based polyurethanes because of their numerous advantages: low toxicity, inherent biodegradability, and high purity. As a result of the hydrophobic nature of triglycerides, vegetable oils produce polyurethanes that have excellent chemical and physical properties such as enhanced hydrolytic tendencies, high tensile strength and elongation, high tear strength, and thermal stability (Oprea, 2010). On the other hand, these materials have relatively low thermal stability, primarily due to the presence of urethane bonds. The onset of

urethane bond dissociation is somewhere between 150 °C and 220 °C, depending on the type of substituents, on the isocyanate and polyol side. Saturated hydrocarbons are known to have relatively good thermal and thermo-oxidative resistance compared to polyether and polyester polyols derived from petrochemicals (Monteavaro, 2005).

In addition to these renewable resources, naturally occurring triacylglycerol (TAG) oils are also significant starting materials for the production of biodegradable polymers. Vegetable oils are abundant and widely available; they are relatively low cost materials and offer a possibility of biodegradable. Polymer prepared from vegetable oils has a number of excellent properties due to the hydrophobic nature of triglycerides. On the other hand; these materials have relatively low thermal stability, primarily due to the presence of urethane bond (Monteavaro, 2005).

They consist of triglyceride molecules that are esters of glycerol and fatty acids, predominantly unsaturated fatty acids. These triglycerides present many reactive sites able to be reacted in order to obtain a product for the polymer industry. This is because triglycerides contain several reactive positions that are amenable to chemical reactions: ester groups, C=C double bonds, allylic positions and the position of ester groups.

Plant oils mainly consist of triacylglycerols (TAG), which can be processed into high-value biochemical for various industries. In polymer application, the conversion of oilseed crops into bioplastics could be a sustainable alternative which could compete with plastics obtained from petroleum chemicals. It has been already shown that polyurethane (PU) produced using vegetable oils such as soybean oil present some excellent properties such as enhanced hydrolytic and thermal stability (Bouzidi *et al.,* 2007).

In recent years, extensive work has been done to develop polymers with triglycerides of fatty acids as the main component. Raw materials from vegetable oils are important sources for green polyols. As a matter of fact, vegetable oils have a number of excellent properties which could be utilized in producing valuable polymeric materials such as epoxy, polyesteramide, alkyd and polyurethane in addition to their many applications in other areas. Other traditional seeds such as linseed, soybean, amaranth, castor, sunflower kernels, cashew nut, and karanja have been used or still under development for the synthesis of different kinds polymeric resin (Velayuthama *et al.*,2009).

Renewable polymer is used to describe the complete mineralization of the starting compound to simpler ones like $CO_2$, $H_2O$, $NO_3$ and other inorganic compounds (Nair, C, I., Jayachandran, K. & Shashidar, S. 2008). Renewable polymer is governed by different factors that include polymer characteristics, type of organism, and nature of pretreatment. The polymer characteristics such as its mobility, tacticity, crystallinity, molecular weight, the type of functional groups and substituents present in its structure, and plasticizers or additives added to the polymer all play an important role in its degradation. During degradation the polymer is first converted to its monomers, and then these monomers are mineralized. Most polymers are too large to pass through cellular membranes, so they must first be depolymerized to smaller monomers before they can be absorbed and biodegraded within microbial cells. The initial breakdown of a polymer can result from a variety of physical and biological forces. Physical forces, such as heating/cooling, freezing/thawing, or wetting/drying, can cause mechanical damage such as the cracking of polymeric materials. The growth of many fungi can also cause small-scale swelling and bursting, as the fungi penetrate the polymer solids.

## 2.3 Formation of polymer foam

In producing and fabricating a good specimen for sound absorption, there is a need to consider the properties of each material chosen, thus the effects on sound absorption material to absorb most of the sound rather than to reflect the sound. There are some materials required to produce sound absorption foam, polyurethane, such as flexible isocyanate, polyol and titanium dioxide ($TiO_2$). The characteristic of polyurethane foam can be changes via adjusting the chemical composition of the raw materials, in particular polyol and isocyanate in which the polyurethane properties mainly depends on the types of polyol such as functionality and hydroxyl value (Lim and Kim 2008).

The forming process of polyurethane foam consist three basic stages such as bubble initiation, bubble growth and cell opening (Klempner and Sendijarevic, 2004). The bubble initiation was initially introduced by physically bending air into the mixture. The bubble growth occurs when the gas diffused and expands the gas phase due to increasing the temperature. The gas may originate from sources such as a gas involved by water reaction, blowing agents, carbon dioxide and surfactant. The

heat generated during the reactions due to exothermic process play an important role in expansion to form a cellular structure. The bubble continued to growth, it will begin the cell opening to produce polyurethane foam.

Polyurethane (PU) foam is produced by one-shot and free rise method (Klempner & Sendijarevic, 2004 and Sung et al., 2007). The one shot and free rise means that the isocyanate, polyol, water and other ingredients are rapidly and intensively mixed and immediately poured to carry out the foaming.

Generally, polyurethane (PU) foams are made via two types of fabrication process which are molded and slab-stock foaming (Zhang, 2008). Moulded foams are largely used in transportation application such as automotive seating whereas slab-stock foams are used in furnishing industry such as mattress and carpet backing (Zhang, 2008). For molded foams, the process begins by mixing all of the reactants together and transferring the foaming mixture to a closed mold (Klempner & Sendijarevic, 2004). The foams are then raised to take on the shape of the mold. However, for slab-stock foams, the process is performed in an open environment (Klempner & Sendijarevic, 2004). That is, the well-mixed reactants are spread onto a conveyor belt, and as the conveyor belt moves forward, the foaming mixture expands and rises to shape.

For the small or laboratory scale production, the polyurethane (PU) foams could be made as a simple hand or cup-foam mixes to techniques of box-foaming mixes according to Klempner & Sendijarevic (2004). In this process, the foam is prepared as free-rise bun. It was noted that the production routes from many laboratory scale foam composite fabrication are actually similar (Table 2.1). The differences between all of the previous works were duration of the components to mix and for the foams to cure. Table 2.1 lists the time consumed at each stage for polyurethane (PU) foam composites production.

Table 2.1: Parameters used for flexible foam composites production

| Year | Author | Preparation of Foam | Foam Cured |
|---|---|---|---|
| 2008 | Sant'Anna *et al.* | i. Polyol and fillers were stirred until completed homogenization.<br>ii. Amine, surfactant, and water were added to mixtures and mechanical stirred for 1 minute.<br>iii. Catalysts was added and stirred for 30 seconds.<br>iv. Isocyanate was introduced to mixtures and stirred for 6 seconds. | The foams were left to cured for three days. |
| 2009 | Mello *et al.* | The foams were produced at room temperature.<br>i. Mechanical stirred the polyol and PET particles for 15seconds.<br>ii. The mixtures, water, silicone, catalysts, and stannous octoate at 850 rpm were again stirred for 1 minute.<br>iii. Addition of isocyanate and methylene chloride to the mixtures and stirred for 5 seconds. | After the foam development, the foam was demould and left to rest for 24 hours. |
| 2009 | Verdejo *et al.* | i. A fixed weight of carbon nanotube was mixed with polyol at 2000 rpm for 10 minutes using an overhead stirrer equipped with dispersion disc.<br>ii. The surfactant, catalyst, distilled water were added to mixtures and mixed at 2000 rpm for 1 minute.<br>iii. Isocyanate was added and stirred for 15 seconds before foaming occurred. | The foam in mould is transferred into oven at 50°C overnight and demould. |
| 2010 | Latinwo., *et al* | i. The mixture of polyol with filler (calcium carbonate) was added to the content of the mixing chamber and stirred for 6 s.<br>ii. The surfactant, catalyst and water as the blowing agent were added to the mixture the polyol and filler in the mixing chamber and thoroughly premixed.<br>iii. The isocyanate was weighed directly into this mixture and the completed formulation was stirred with an overhead mechanical mixer for 4 s.<br>iv. The foam was poured in open mould which was treated with mould release agent to produce with free-rise foam | After 10 min the foams is removed from the mould and left to cure for at least 7 days |

Table 2.1: (Continued)

| | | | |
|---|---|---|---|
| 2011 | Ting *et al.* | i. The desired fumed silica was mixed with isocyanate using a magnetic stirrer for 30 minutes.<br>ii. Polyol with catalyst, surfactant and blowing agent contain were added into mixture and stirred at 500 rpm for 15 seconds. | The foams is transferred into an oven at 50°C for 3 hours and demould. |
| 2012 | Bernal *et al.* | i. The polyol and carbon nanofillers were stirred using overhead stirrer equipped with dispersion disc for 6 hours and 2400 rpm.<br>ii. The surfactant, catalysts, and distilled water were added to mixtures and stirred at 2400 rpm for 3 minutes.<br>iii. Finally, isocyanate was added and mixed again for 20 seconds. | The foaming process occurred in an open mould |

### 2.3.1 Foam Formula and Generation

Foam is an important engineering material. It offers unique advantages in terms of low cost and weight, easy to manufacture and has good energy absorption properties. It is used in many applications; acoustic absorption, impact retardation and mechanical damping (Singh *et al*., 2003 and Lee *et al*., 2007).

In most modern automotive seats, static comfort and vibration isolation are now achieved through the use of foam alone. Polymer foams represent one of many types of polymeric materials such as solid (nonporous), reinforced, laminated, etc. Schematically in Table 2.2, all types of polymer foam can be classified in three generations and each type of foam has different technical characteristics and also different cellular structure (Klempner and Sendijarevic, 2004).

Table 2.2: Three generation of polymer foams

| Generation | Type of Foam |
|---|---|
| First Generation:<br>1940-1970 | Isotropic foams<br>Sandwich structures |
| Second Generation:<br>1970-1985 | Structural (Integral) foams<br>Syntactic foams<br>Reinforced and filled foams<br>Foamed laminates<br>RIM and RRIM foams<br>Microcellular foams |
| Third Generation:<br>1985 until present | One-sided structural foams<br>Inverse structural foams<br>Syntactic - structural foams<br>Foamed syntactic foams<br>Foamed fibres and films<br>Macro/Micro (bi – modal) fomas<br>Foam-in Foam structure<br>Nano foams |

Basically, polyurethane (PU) foam is made from a formula that contains a host of ingredients selected to aim in achieving the desired grade of foam. These components included polyol, isocyanate, water, catalysts, surfactants, cross-linkage agent, auxiliary blowing agent, and additives such as colorant, flame retardant, antistatic agent, bacteriostat or UV stabilizer. Among all, polyol and isocyanate are the main components used to forms polyurethane linkage (Figure 2.6).

$$R-N=C=O + R'-CH_2-OH \rightarrow R-N-\underset{\underset{H}{|}}{C}-N-\underset{\underset{H}{|}}{R'}$$

Isocyanate Alcohol Urethane

Figure 2.6: Gelation reaction or PU cross-linkage reaction (Kaushiva, 1999)

The reaction between polyol and isocyanate is called gelation reaction (Kaushiva, 1999). It is an exothermic process for which heat of reaction had been reported approximately 24 kcal/mol of urethane (Klempner & Sendijarevic, 2004).

There is another reaction occurred during foam generation. It is called blow reaction (Kaushiva, 1999).

$$R-N=C=O+H_2O \rightarrow R-\underset{\underset{H}{|}}{N}-C=O-OH \rightarrow CO_2+R-NH_2+\text{Heat}$$

Isocyanate Water Carbamide Acid Carbon Dioxide Amine

Figure 2.7: Blow reaction between isocyanate and water (Kaushiva, 1999)

Figure 2.7 illustrates the blow reaction generation. In this reaction, water reacts with isocyanate to produce carbon dioxide ($CO_2$) which diffuses to the existing gas bubbles in the polyol and so expands the foam. It was reported that the internal temperature of foam bun/rise would build up on the order of 140 °C during foam generation (Klempner & Sendijarevic, 2004)

Other components in formula are working as: surfactants are necessary components in foam formation in order to produce a well open-celled morphology. They perform to reduce surface tension in polyurethane, emulsifying incompatible ingredients, promoting bubble nucleation, stabilizing the rising foam, thus reducing the deformation effect and the most important is to stabilise the cell wall.

As reported by Klempner & Sendijarevic (2004), surfactant prevents the coalescence of rapidly growing cells until those cells have attained sufficient strength through polymerization to become self supporting. Without this, cell coalescence would lead to a total foam collapse. Catalysts are generally used in foam formulation for establishing a balance between the chain propagation in of gelation reaction and blow reaction (Klempner & Sendijarevic, 2004). Besides, it is also for assuring completeness of reaction or “cure” in finished foam (Klempner & Sendijarevic, 2004).

There are three basic stages found in foam foaming process. They are bubble initiation, bubble growth, and cell opening (Klempner & Sendijarevic, 2004). Figure 2.8 illustrates the development and formation of a polyurethane (PU) foam in an open-mould. The first stage is the bubble initiation of foam is started by introducing the physical blending air into the mixture. This could be done by using a high shear

mixing machine or a stirring device that works in a certain rotational speed for entrance of enough bubbles to account for all of the cells present in the PU foam (Latinwo *et al*., 2010a and Zhang *et al*., 2011).

The second stage is called bubble growth. This occurs when the gas diffuses and expands the gas phase due to the increase in foaming temperature. The gas may originate from sources such as gas evolved by water reaction, as the gas dissolves in the liquid reactant, auxiliary blowing agents vaporizes and gas evolves by thermal decomposition of additives or components (Kaushiva, 1999). According to the Figure 2.4, the gas diffuses to bubbles which is carbon dioxide ($CO_2$). The heat generated during the reactions (exothermic process) play an important role in expansion for example $CO_2$ to form a cellular structure.

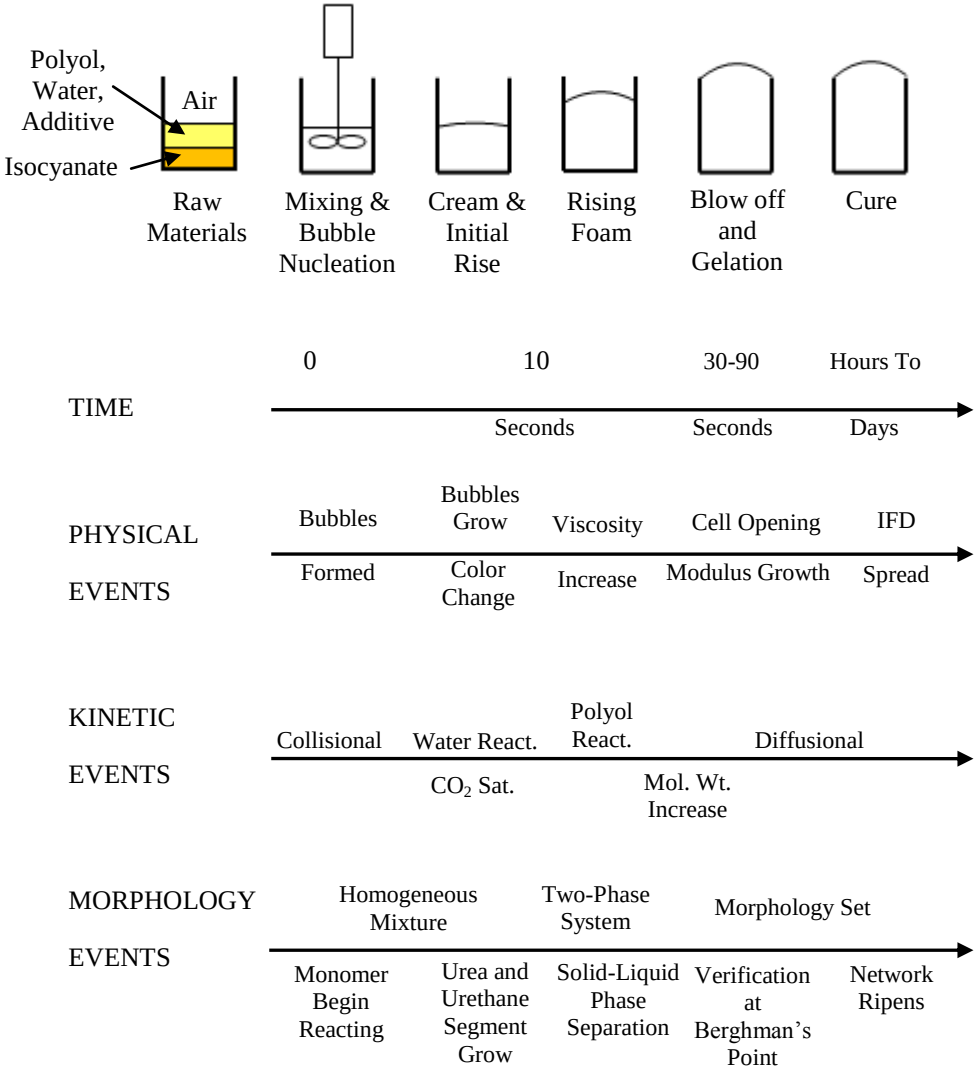



Figure 2.8: Development of polyurethane (PU) foam (Klempner & Sendijarevic, 2004)

It was noted that as bubbles continued to grow, it will begin to impede with each other in the foam system (Kaushiva, 1999). At this time, the solid phase of matrix is forced to distribute itself around and form as lamellae and plateau borders in between the cells.

This solid phase can be referred to the Figure 2.9 which illustrates the morphology of cured polyurethane (PU) foam. From this figure, there is a polyhedrons development inside foam (Kaushiva, 1999). It was reported that the bubbles packaging during foam rising is very incontrollable (Kaushiva, 1999). Hence, the cellular-structure of foam may shows anisotropic. Gibson & Ashby (1997) mentioned that almost all man-made foams are anisotropic.

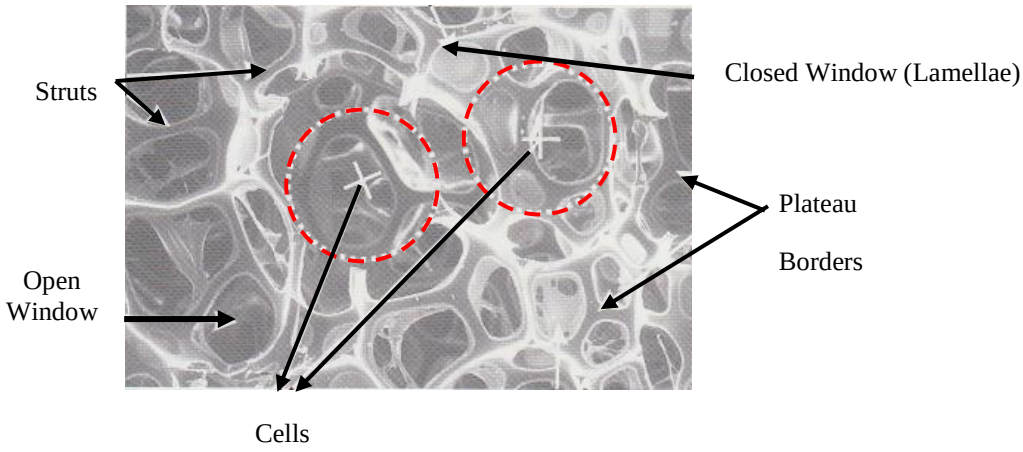



Figure 2.9: Morphology of polyurethane (PU) foam (Klempner & Sendijarevic, 2004)

In the third stage which is the cell opening, closed cells started to open when one or more bubbles rupture. These ruptures are actually caused by excessive thinning of lamellae which could not withstand the pressure in the cell. Struts are formed once the lamellae of closed cell rupture. At the end, the open-celled polyurethane (PU) foam is obtained once the foam finish is cured. However, it is not easy to obtain well open-celled foam due to problems like blowing agents escape in close cells, which may result in the cells remaining closed at all the time (Kaushiva, 1999).

In order to produce well open-celled foams, there are two critical elements to meet, which are adjustment of (i) the rate of foaming, and (ii) the rate of